Inorganica Chimica Acta, 43 (1980) 65–67
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Chemistry of Uranium.
Part 31. The Kinetics of the Reaction between Ce(IV) and U(IV) in Acetone

J. G. H. DU PREEZ, H. E. ROHWER* and D. C. MORRIS
Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, South Africa

Received April 21, 1980

The reaction between U(IV) and Ce(IV) has been studied in acetone. It was found to be 1st order with respect to both reactants and second order overall. The activation parameters have been evaluated.

The mechanism was not studied, but it is postulated that the reaction is between oppositely charged species in contrast to that found in aqueous solution.

Introduction

The reaction between Ce(IV) and U(IV), in acetone, proceeds at a rate which is measurable using conventional kinetic techniques in contrast to that in aqueous solution [1–3].

Little work on the kinetics of redox reactions has been carried out in non-aqueous media mainly because of the difficulty of explaining such results. The role of the solvent on the kinetics is uncertain with possible contributions from variables such as dielectric constant, polarity, solvation, viscosity, ionisation effects and acidity of the solvent. That a lot of these factors are interrelated does not make the problem any easier.

Much work has been done in this laboratory on the chemistry of uranium and cerium in acetone [4, 5] and despite the above mentioned difficulties it was thought that the kinetics of the reaction between U(IV) and Ce(IV), in acetone, should be studied and the thermodynamic quantities determined even if these could not at present be meaningfully compared with those obtained in an aqueous medium.

Experimental

The experiments were carried out in a controlled temperature room where the temperature was held at the required value with a variation of ±0.1 °C. It was decided to do the experiments in this way because of the difficulties encountered when the water bath and water jacketted cells were used in a normal environment where, although the temperature control of the water bath was ±0.01 °C, the heat capacity of acetone is so low that a temperature rise of several degrees was noted in the short time required for transfer of the solution from the bath to the cell.

The acetone was analar grade. The Ce(IV) compound was $CeCl_4 \cdot 2ipa$ (ipa = diisopropylacetamide).

Conductometric titrations have shown that, in acetone, ipa does not coordinate strongly to $CeCl_4$ [5] and so it is assumed that $CeCl_4 \cdot 2ipa$ in a dilute acetone solution can be approximated to a pure $CeCl_4$ solution in acetone.

The U(IV) compound used was UCl_4 and was prepared by the reductive chlorination of UO_3 by hexachloropropene [6].

The U(IV) was determined by pipetting a known volume into an excess of acidified ferric ammonium sulphate solution and the Fe(II) produced determined by titration with a standard potassium dichromate solution. The titration was performed potentiometrically using a Metrohm E536 potentiograph with a combined platinum electrode to determine the end point.

The Ce(IV) was determined, for standardisation purposes, by pipetting a known volume into excess acidified standard Fe(II) solution and the remaining Fe(II) titrated with potassium dichromate as described above. The standardised Ce(IV) solution was then used to determine the extinction coefficient of Ce(IV) at a wavelength of 400 nm using a Beckman Acta MVII so that the variation of Ce(IV) with time could be followed spectrophotometrically. It was found that U(IV), U(V), U(VI) and Ce(III) do not absorb at a wavelength of 400 nm using the experimental concentrations which were of the order of 3×10^{-4} mol dm^{-3}.

2 cm^3 of the Ce(IV) solution were pipetted into a 3.5 cm^3 cell and 1 cm^3 of the U(IV) solution added using a syringe. The cell was shaken vigorously and placed into the spectrophotometer. The reaction could normally be followed approximately 10

---

*Author to whom correspondence should be addressed.

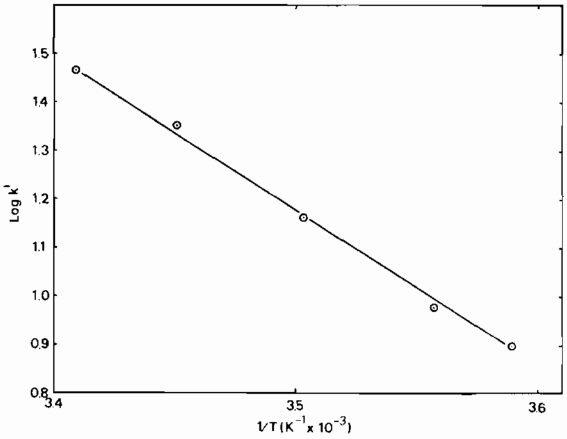

Fig. 1. The variation log(Ce(IV)/U(IV)) with time at different temperatures.

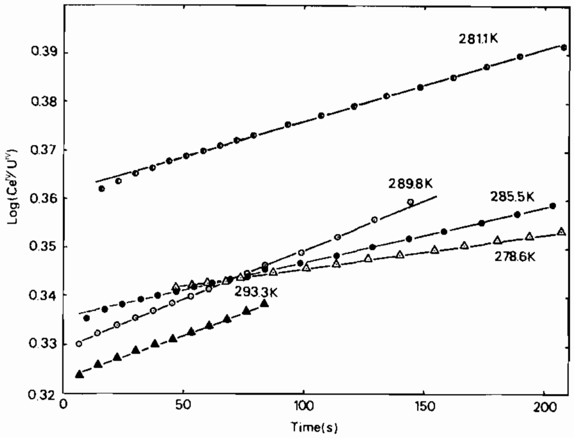

Fig. 2. The variation of the apparent second order rate constant with the reciprocal of the absolute temperature.

seconds after the addition of the U(IV). All solutions were prepared immediately prior to use.

It is known that Ce(IV) can oxidise acetone [7, 8], but investigations have shown that the rate of the reaction is appreciably slower than the Ce(IV)–U(IV) reaction and its effect on the rate of reaction can be ignored. All the results obtained were subjected to a least squares treatment.

Results and Discussion

The extinction coefficient, ϵ, for Ce(IV) at a wavelength of 400 nm was found to be 2070 ± 50 $dm^3\ mol^{-1}\ cm^{-1}$ and obeyed Beers Law up to an absorbance of 2. The reaction was found to be stoichiometric, *i.e.* 2 mol of Ce(IV) react with 1 mol of U(IV), and Ce(III) and U(VI) did not influence the rate of reaction using the experimental concentrations.

The order of reaction was deduced in the following way:

The apparent second order rate constant, k', is defined by eqn. (1)

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{-2d[\mathrm{U(IV)}]}{dt} = -2k'[\mathrm{U(IV)}][\mathrm{Ce(IV)}] \qquad (1)$$

if $[\mathrm{U(IV)}]_o$ and $[\mathrm{Ce(IV)}]_o$ represent the concentrations of U(IV) and Ce(IV) at zero time then the concentrations of reactants and products are given by

$$[\mathrm{U(IV)}] = [\mathrm{U(IV)}]_o - 0.5[\mathrm{Ce(IV)}] \qquad (2)$$

$$[\mathrm{Ce(IV)}] = [\mathrm{Ce(IV)}]_o - [\mathrm{Ce(III)}] \qquad (3)$$

Substitution of eqns. (2) and (3) into (1) and integration in terms of Ce(III) gives

$$k't = \frac{2.303}{[\mathrm{Ce(IV)}]_o - 2[\mathrm{U(IV)}]_o}\log\frac{[\mathrm{Ce(IV)}]}{[\mathrm{U(IV)}]} + C \qquad (4)$$

where C is an integration constant related to the initial concentration of reactants.

Equation (4) indicates that a plot of log [Ce(IV)]/[U(IV)] *vs.* time should yield a straight line of slope = $2.303/k'([\mathrm{Ce(IV)}]_o - 2[\mathrm{U(IV)}]_o)$ if the reaction is of first order in [Ce(IV)] and [U(IV)]. Such plots, for different temperatures, are shown in Fig. 1. The plots gave good straight lines up to 75% completion of the reaction. In certain cases slight curvature was noted in the early part of the reaction and this is attributed to inefficient mixing of the reactants. The order of reaction in the present case, in acetone, is similar to that found in aqueous solution [1]. The experiments were performed in triplicate at each temperature and the average rate constant used in the Arrhenius plot shown in Fig. 2. The rate constants, at a particular temperature, varied by approximately 5%.

The energy, enthalpy and entropy of activation were found to be 11.7 ± 1.2 kJ mol^{-1}, 9.5 ± 1.0 kJ mol^{-1} and −182 ± 18 kJ mol^{-1} respectively.

The mechanism of the reaction was not studied, however, some observations deserve comment. It has been suggested that autoionisation of UCl_4 occurs in acetone [9] *e.g.* $2UCl_4 \rightleftarrows UCl_3^+ + UCl_5^-$ with the ionic species being 60% of the total species present. Autoionisation is preferred to ionisation mainly because of the low dielectric constant of acetone which will favour a large anionic species (*e.g.* UCl_5^-) with diffuse charge density to a small species (*e.g.* Cl^-) with high charge density.

Conductometric titrations of $CeCl_4$·2ipa, in acetone, have shown that it behaves in an analogous manner to UCl_4 [5], *i.e.* extensive autoionisation occurs. Thus in acetone oppositely charge species of U(IV) and Ce(IV) are present, and it is between these species that one would expect the reaction to occur, *e.g.* $CeCl_5^- + UCl_3^+ \rightarrow$ products, and/or $CeCl_3^+ + UCl_5^- \rightarrow$ products. This is in contrast to the mechanism proposed in an aqueous medium [1] where the reaction is assumed to be between cationic species.

In the light of the above it is difficult to account for the negative entropy of activation since this cannot be explained in terms of electrostriction of the acetone molecules because of the opposite sign of the charges on the reacting species. An inner sphere mechanism, with a highly ordered intermediate complex, could account for the negative entropy of activation.

Frolova *et al.* [10] have found that an increase in acetone concentration increases the rate of reaction between cationic species of U(IV) and Fe(III) in aqueous solution, which is contrary to the effect expected from coulombic considerations (*i.e.* a reduction in dielectric constant should reduce the rate). They explain this by suggesting that the redox reaction occurs by 'long distance' electron transfer and that coulombic effects at this range are negligeable. To support this they showed that after addition of a certain amount of acetone the rate dropped which they attributed to the breakdown of intermolecular bonding between the water molecules thereby reducing the possibility of 'long distance' electron transfer.

Their mechanism, however, considered only cationic species and it is possible that as the acetone was added the nature of the species changed thereby changing the mechanism which would make it difficult for useful comparisons to be made.

Acknowledgement

The authors wish to acknowledge the financial assistance received from the South African Council for Scientific and Industrial Research, the South African Atomic Energy Board and the University of Port Elizabeth.

References

1 F. B. Baker, T. W. Newton and Milton Kal, *J. Phys. Chem.*, *64*, 109 (1960).
2 Y. A. El-Tantawy and A. I Abu Shady, *Z. Phys. Chem.*, *84*, 225 (1973).
3 P. Michaille and T. Kikindai, *J. Inorg. Nucl. Chem.*, *39*, 859 (1977).
4 J. G. H. du Preez, B. J. Gellatly, M. L. Gibson, D. R. Groot and H. E. Rohwer, *J. S. Afr. Chem. Inst.*, *29*, 105 (1976).
5 P. J. Wright, M. Sc. Thesis, *University of Port Elizabeth, (1979).*
6 *J. A. Harman and J. F. Suttle, Inorg. Synth.*, *5*, 143 (1957).
7 J. Shorter and C. Hinshelwood, *J. Chem. Soc.*, 3276 (1950).
8 J. Shorter, *J. Chem. Soc.* 1868 (1962).
9 D. R. Groot, *Ph.D. Thesis University of Port Elizabeth (1978).*
10 L. M. Frolova, G. A. Rimofeev and A. G. Rykov, *'Proceeding of the Moscow Symposium of Transuranium Elements'*, Eds. V. I. Spitsyn and J. I. Katz, Pergamon, 1976, pp. 127–130.